IS-5178

AMES LABORATORY

On-Line Sensor System for Monitoring the Cure of Coatings on Glass Optical Fibers. Phase II: Application of the Sensor System to On-Line Molecular Analysis Needs in Other Industries of the Future

Final Report

By Roger W. Jones and John F. McClelland

Performance Period: May 20, 2002 to September 30, 2005

November 2005

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Prepared for the U.S. Department of Energy under Contract W-7405-Eng-82

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Executive Summary

Molecular spectroscopic methods have become popular for on-line analysis, but solid and viscous-liquid process streams present a problem because they have high absorption coefficients (i.e., are nearly opaque) in the mid-infrared region, which is rich in compositional information. That means only a very thin layer can be analyzed by conventional transmission spectroscopy, where the infrared radiation is passed through the material being analyzed. Most solid and viscous-liquid process streams cannot be analyzed on line using conventional mid-infrared spectroscopy techniques. We have developed an on-line, mid-infrared, molecular-analysis sensor system based on Transient InfraRed Spectroscopy (TIRS), which avoids the opacity problem. The present project expands the application of TIRS beyond the scope of the Phase I project. TIRS was demonstrated on the process lines of three different organizations. TIRS was used to monitor the composition of polymer extrusions on a compounding line at GE Plastics, to monitor simultaneously the individual thicknesses of two polymer layers applied at the same time to a paper substrate on a coating line at Eastman Kodak Company, and to monitor the tensile strength of a soy protein/rubber polymer extrusion at the Center for Crops Utilization Research at Iowa State University. In all three cases, analytically useful mid-infrared spectra were acquired on line and in real time from the process streams.

Introduction

Molecular spectroscopic methods have become popular for on-line analysis.[1,2] The mid-infrared region (400 to 4000 cm^{-1}) is particularly rich in compositional information, and commercial, on-line, mid-infrared sensors are available for gaseous and liquid process streams. Solid and viscous-liquid process streams, however, present a problem. Most have high absorption coefficients (i.e., are nearly opaque) in the mid-infrared, so only a very thin layer can be analyzed by conventional transmission spectroscopy, where the infrared radiation is passed through the material being analyzed. Reflection spectroscopy, in which the infrared radiation reflected off the process stream is measured, is applicable only when the process-stream material has the proper surface characteristics. Most solid and viscous-liquid process streams cannot be analyzed on line using conventional mid-infrared spectroscopy techniques.

An on-line, mid-infrared, molecular-analysis sensor system has been developed based on Transient InfraRed Spectroscopy (TIRS), which avoids the pitfalls of conventional approaches.[3,4] In the earlier, Phase I project, TIRS was applied to monitoring the cure of coatings on glass optical fibers.[5] The present project expanded the application of TIRS to on-line monitoring of other polymer-based processes. This involved three separate collaborations between Ames Laboratory (principal investigator John McClelland) and three industrial and academic groups. Each of these collaborations included testing TIRS operation on their pilot processing line. TIRS was used to monitor the composition of polymer extrusions on a compounding line at GE Plastics (Mt. Vernon, IN), to monitor simultaneously the individual thicknesses of two polymer layers applied at the same time to a paper substrate on a coating line at Eastman Kodak Company (Kodak Park, Rochester, NY), and to monitor the tensile strength of a soy protein/rubber polymer extrusion at the Center for Crops Utilization Research (Iowa State University, Ames, IA). In all three cases, analytically useful mid-infrared spectra were acquired on line and in real time from the process streams. Ultimately, the TIRS output could be linked to process control either directly, via automatic feedback control, or by alerting the human operators through a visual display or an alarm.

TIRS Methodology

TIRS is based on emission spectroscopy. All materials spontaneously emit infrared light by virtue of their temperature. The hotter they are, the stronger they emit. In conventional emission spectroscopy, a sample is warmed until it emits sufficient infrared light, and then the emission spectrum is recorded. Thin, warm materials emit primarily at the same wavelengths that they primarily absorb when infrared light is passed through them, so the analysis is identical to conventional transmission spectroscopy, which has been a mainstay in analytical laboratories for decades. Fortunately, materials need be only a few tens of degrees above ambient temperature to emit sufficiently in the infrared. Unfortunately, if a warm sample is too thick, it emits at all wavelengths, producing a featureless, blackbody spectrum. TIRS is innovative in that it avoids this blackbody problem without the sample being physically thinned.

TIRS uses a temperature gradient to isolate spectroscopically a thin surface layer of the moving solid material, thereby circumventing the blackbody problem. Figure 1 shows schematically how TIRS works. The moving process stream passes through the field of view of an infrared spectrometer. As it does so, a small jet of either hot or cold air strikes it, warming or cooling the surface. For materials at ambient or lower temperature, a hot-air jet is normally used. The resulting heated surface layer acts as a thin emission source separate from the rest of the process stream. Because it is thin, it produces a structured, analytically useful spectrum, which the spectrometer records. Because the material is moving, the heated layer is carried out of the spectrometer field of view before it can thicken and cool appreciably. The spectrometer therefore observes the infrared emission from a heated layer that seems to stay perpetually thin. For materials well above ambient temperature, a cooling jet is used. This produces a thin, cool layer at the surface of the material. Emission from the cooled layer is reduced because of the lowered temperature, but the uncooled bulk of the material below the surface layer continues to produce a blackbody emission. The emission from the bulk passes through the cooled layer before it is observed by the spectrometer. The thin, cooled layer therefore acts as a conventional transmission-spectroscopy sample, absorbing radiation primarily at its characteristic wavelengths, so the spectrometer observes a structured transmission spectrum of the cooled layer. As in the hot-jet version, the motion of the material keeps the cooled layer thin within the spectrometer field of view.

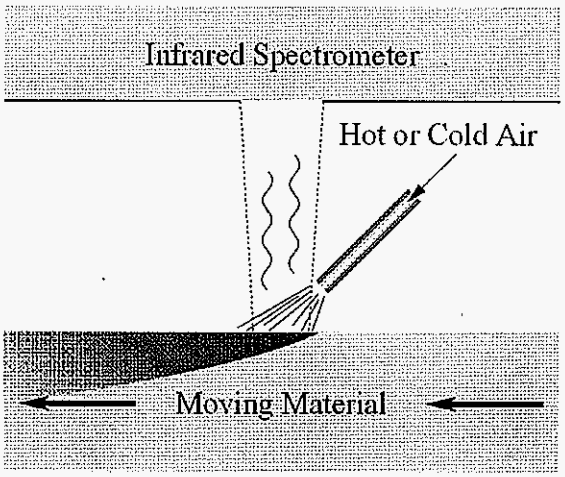

Figure 1. Schematic of TIRS.

The acquired spectra are analogous to conventional spectra, so the same methods and tools developed for laboratory spectroscopy can be applied to TIRS spectra for chemical analysis. The technical aspects of TIRS are described in more detail elsewhere.[3,4] TIRS is effectively a noncontact probe because only a stream of air needs to contact the material on the process line. Other applications of TIRS have been documented elsewhere.[3-7] Patents on TIRS are held by the Iowa State University Research Foundation.[8]

All of the on-line tests performed in this project used a TIRS unit consisting of a Bomem MB100 FT-IR spectrometer, with a liquid-nitrogen cooled MCT detector and fitted with a TIRS "front end," which consists of an external mirror or optics chain to collect the infrared radiation from the process web and an adjustable mount holding a hot-air tool or cooling-air nozzle to provide the heating or cooling air stream.

Partial-least-squares (PLS) chemometrics was used to correlate the TIRS spectra with the process-stream property being measured and thereby calibrate the monitor.[9,10] In PLS, a training set of TIRS spectra for which the process-stream property has known values (determined by off-line means) are provided to the PLS algorithm, which correlates property changes with spectral changes, producing a model that can provide real-time analysis of subsequent spectra of webs with unknown values of the property being measured. Because of time limitations during the on-

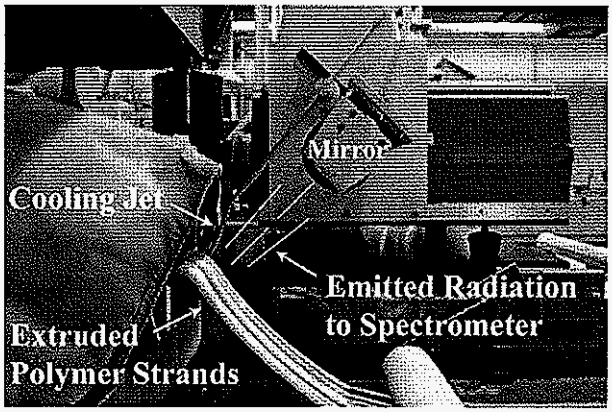

Figure 2. TIRS unit monitoring composition of molten polymer strands exiting extruder during on-line tests at GE Plastics.

line tests, no separate validation set of spectra was acquired to test the accuracy of the TIRS/PLS models. Instead a cross-validation process was used. In a cross validation, one of the training set members is removed and a PLS model is built without it. The spectrum held out is tested as an unknown with the model, and the property value predicted by the model is recorded. The held out spectrum is then put back in, another training-set member is removed, and the process is repeated. This continues until all members of the training set have been removed and tested as unknowns. The accuracy of the model can be assessed from plots of predicted versus actual compositions and from statistical measures of these quantities, such as the standard error of cross validation (SECV), which is the root-mean-square difference between the predicted and actual values.

Once a PLS calibration has been created, it is possible for the TIRS monitor to provide property values in real time. In this project, time limitations prevented carrying out separate calibration runs to generate PLS training sets, so cross validations created after the on-line data acquisitions were completed were used to judge the quality of the results. There is no technical barrier, however, to real-time property-value determinations using TIRS.

Collaboration with GE Plastics

The on-line tests performed at GE Plastics in July 2004 involved monitoring the composition of polymer-blend strands as they exited an extruder. These molten strands were monitored using the cooling-jet version of TIRS. Figure 2 shows the TIRS unit mounted on a GE Plastics pilot extruder line during the tests. Six polymer strands exit the extruder and drop into a water bath at the bottom of the picture. The angled tube just above where the strands exit from the extruder directs the cooling jet so that it strikes one of the strands as it passes through the spectrometer field of view. The collection mirror is visible to the right of the tube, but several inches away from the polymer strands. It is aimed at a 45° angle to view the cooled strand just after the air jet strikes it.

Two different sets of polymer blends were run through the extruder and analyzed with the TIRS unit. One set consisted of binary blends of polycarbonate and polyester at various concentrations ranging from pure polycarbonate to pure polyester. The second set consisted of ternary blends of polycarbonate, polybutylene terephthalate (PBT), and acrylonitrile/butadiene/styrene rubber (ABS), ranging from 20 to 70 weight percent polycarbonate, from 20 to 70 weight percent PBT, and from 0 to 30 weight percent ABS. During the extrusion of the binary blends, grab samples was taken for later NMR-based compositional analysis performed by GE Plastics. The NMR results were used as the reference values for the PLS modeling and calibration for the binary

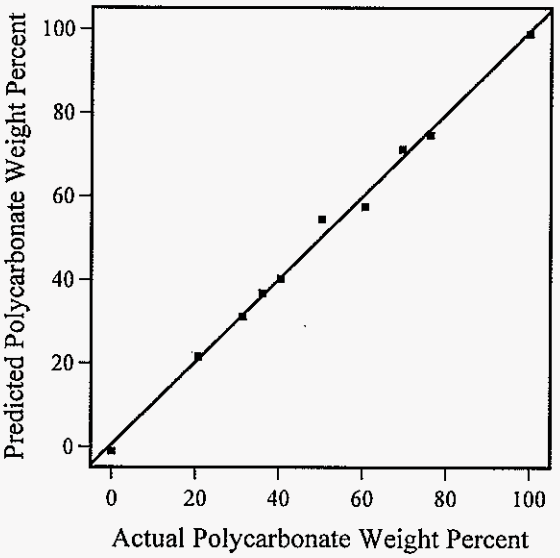

Figure 3. PLS cross-validation results from on-line TIRS analysis of polycarbonate/polyester extrusion.

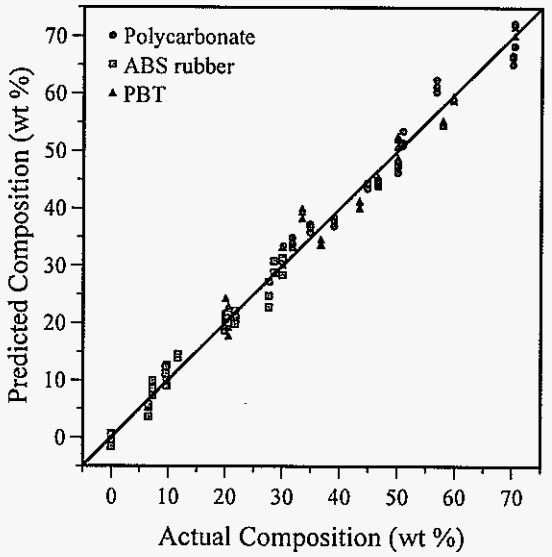

Figure 4. PLS cross-validation results from on-line TIRS analysis of polycarbonate/PBT/ABS rubber extrusion.

blends given here. Reference values for the ternary blends were the weighed compositions of the feedstocks for the blends.

Figure 3 shows a plot of the TIRS-based compositions for the binary-blend samples from the PLS cross validation versus the NMR analyses. The standard error of cross validation (SECV) is 1.92 weight percent. The line is a linear-regression fit of the analyses (predicted = 0.49 wt % + 0.99 × actual), which is very close to ideal (predicted = actual). The TIRS analyses are very accurate. Figure 4 plots the TIRS-PLS cross validation results versus actual compositions for the three components of the ternary blends. The SECVs are 2.4 wt %, 2.6 wt %, and 1.7 wt % for polycarbonate, PBT and ABS rubber, respectively. These results are slightly less accurate than those for the binary blends, reflecting the more complex spectroscopy and mathematics of a three-component system. Nevertheless, the results are still very good.

Collaboration with Eastman Kodak Company

The on-line tests at Kodak occurred in May 2004. They used the heating-jet version of TIRS. During those tests, a polymer bi-layer from a pair of extruders was applied to a coated-paper substrate. The bi-layer consisted of a top layer and a tie layer between the top layer and the substrate. Two series of test measurements were made. The first series consisted of measurements taken on the web at a variety of line conditions that produced various thicknesses of the individual layers being applied. The goal was to see if the TIRS unit could be calibrated to measure simultaneously both of these individual layer thicknesses. The second test series consisted of measurements taken at equally spaced points along the width of the web under a single set of line conditions to see what the TIRS measurements could reveal about the expected cross-web changes in layer thicknesses.

Figure 5 shows the TIRS unit mounted on a Kodak pilot line during the on-line test. The bulk of the unit is the Bomem spectrometer. The small, angled nozzle directly over the web at the front of the TIRS unit directs the stream so that it strikes the web as it passes over the top of the roller in the foreground. The collection mirror is in the overhanging structure above the nozzle. The whole TIRS unit was mounted on a pair of slides that allowed it to be moved across the web while operating so that measurements could be taken at various points along the web width.

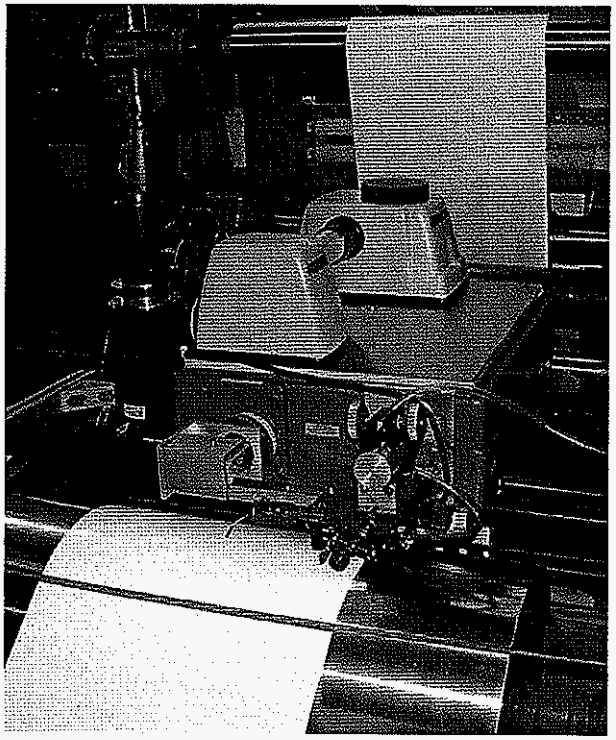

Figure 5. TIRS monitor on pilot line at Kodak.

In the first series of measurements, line speed was varied from 600 to 800 ft/min, and extruder speeds were varied to produce top-layer thicknesses corresponding to coverages ranging from 3.3 to 6.7 g/m^2, and tie-layer coverages from 0.8 to 1.6 g/m^2, producing total bi-layer coverages from 4.1 to 8.3 g/m^2. A single TIRS measurement was made at each of 30 different line conditions. The Bomem spectrometer acquires a complete spectrum in 0.8 s (at 8 cm^{-1} resolution), but to improve measurement precision, eight scans were summed for each TIRS measurement, so each measurement took 6.4 s. A short experimental run immediately after the TIRS unit was first mounted on the line showed that eight scans provided an optimum balance between spectrum reproducibility and temporal (and therefore spatial) resolution. Increasing the number of scans only modestly increased the reproducibility. The web travels between 64 ft (at 600 ft/min) and 85 ft (at 800 ft/min) during an eight-scan measurement, so these constitute the along-the-web resolution under these conditions. Cross-web resolution would depend on whether the TIRS unit was fixed in place or moved by a scanner during use.

Figures 6 through 8 show plots of the TIRS-PLS predicted versus actual coverages for the top and tie layers separately, as well as for their combination, using the most accurate PLS model developed for each. The SECVs are 0.17 g/m^2 for the top layer, 0.09 g/m^2 for the tie layer, and 0.25 g/m^2 for the total coverage. These are very good accuracies when compared to the range of coverage values included in the series of measurements. From Figure 7, it may seem that the tie-layer measurement is intrinsically less accurate than the others, but it may have been limited by the actual-coverage values provided by Kodak staff. The actual-coverage values were provided only to 0.1 g/m^2 precision, thus any calibration built on these numbers will be limited to an accuracy of no better than about 0.1 g/m^2. The actual values used in the model were derived from direct weighing of the total coating applied and from the speeds of the two extruders. Samples from a subset of the line conditions were subjected to microscopic examination by Kodak staff after the test run to provide a better set of actual values for the calibration, but these measurements proved problematic. Tie layer thicknesses in a sizeable fraction of the samples

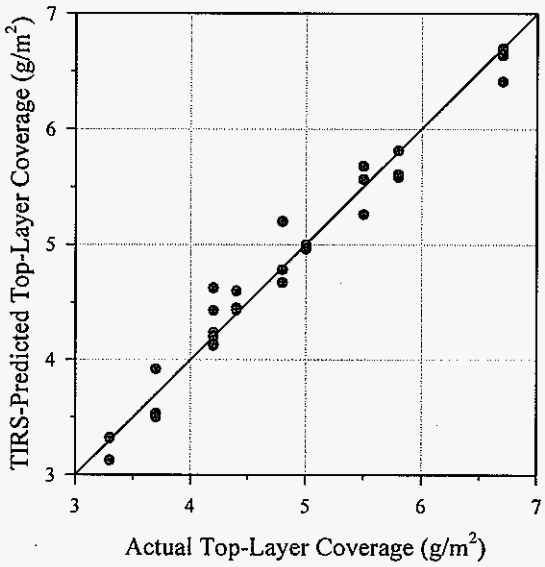

Figure 6. PLS cross-validation correlation of TIRS measurement of top-layer thickness and known thickness.

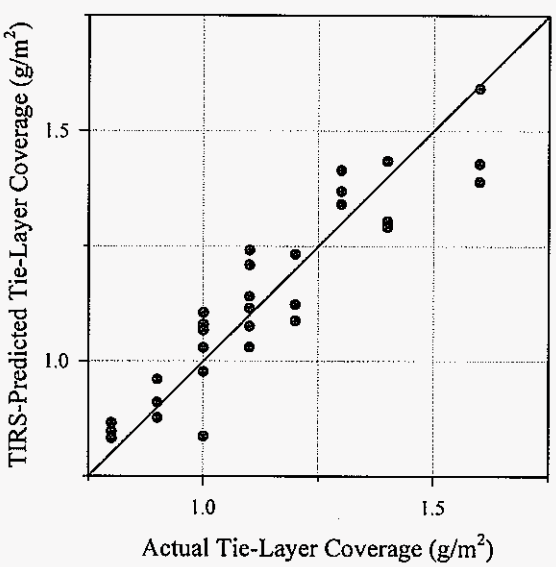

Figure 7. PLS cross-validation correlation of TIRS measurement of tie-layer thickness and known thickness.

were not reported because the layer was too thin to measure by optical microscopy. The TIRS monitor could measure thicknesses that microscopic examination could not resolve.

The second series of measurements was concerned with measuring how the layer thicknesses varied across the width of the web. TIRS spectra were acquired at equally spaced points along the web width while the pilot line was running at 100 ft/min. This lower line speed was used because of a limited amount of substrate stock available for coating. Unfortunately, this speed was so much lower than that used for the first set of measurements that the calibration generated there could not be used to analyze the spectra from this second series. The results of this cross-web test are therefore only qualitative in nature. The largest effect on the TIRS spectra was not directly related to layer thicknesses. The TIRS spectra clearly showed a variation in temperature across the web, with the center being approximately 10 °C hotter than the edges of the coating. This makes the observed TIRS spectra stronger at the center of the web. Using peak-intensity ratios from the TIRS spectra avoids any interference from this temperature variation across the web.

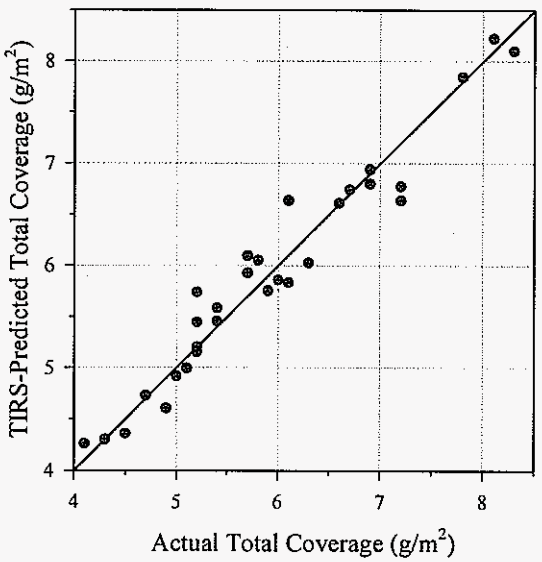

Figure 8. PLS cross-validation correlation of TIRS measurement of total (top and tie layers) thickness and known total thickness.

The process-line web was 14 inches wide, but only the central 11 inches were coated, so

measurements were taken at one-inch increments across the web at distances of 2 to 12 inches from one edge of the web. Spectrum peaks at 1250 and 833 cm^{-1} were found to come solely from the top layer of the web material. Similarly, a peak at 1115 cm^{-1} came solely from the tie layer, and peaks at 1377 and 667 cm^{-1} came just from the substrate. Ratios of the heights of various pairs of these peaks therefore are a qualitative measure of the top and tie layer thicknesses.

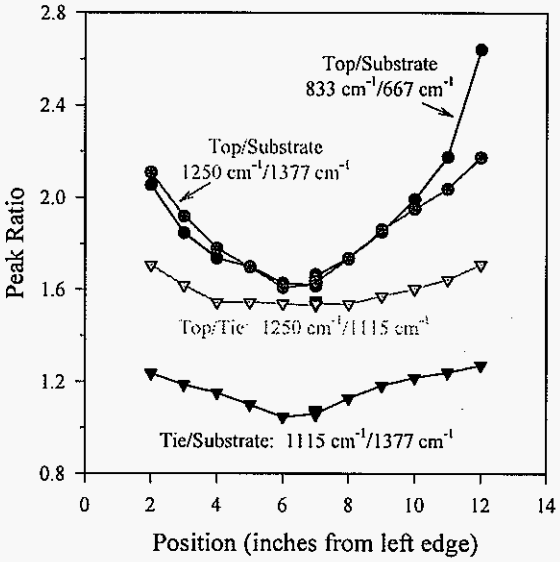

Figure 9. Peak-height ratios for peaks arising from top layer, tie layer, and substrate, showing dependence of layer thicknesses on position along width of web. The 833 cm^{-1}/667 cm^{-1} ratio has been scaled by a factor of 0.87.

Figure 9 shows plots of the ratios of the heights of these top-layer, tie-layer, and substrate peaks with one another. The two top-layer/substrate ratios (833 cm^{-1}/667 cm^{-1} and 1250 cm^{-1}/1377 cm^{-1}) have the same general shape, with a minimum at 6½ inches and the slope continuously increasing with distance away from that point. This implies that the top layer is thinnest near 6½ inches and thickens at first slowly but ever more quickly with distance away from that point. This shape can be taken as a reference for comparison to the other two curves. The top-layer/tie-layer ratio (1250 cm^{-1}/1115 cm^{-1}) is flat in the middle and rises toward the edges, and the tie-layer/substrate ratio (1115 cm^{-1}/1377 cm^{-1}) is curved at the center, like the top-layer/substrate ratios, but flattens toward the edges. This implies that the tie layer has a profile similar to that of the top layer near the center of the web, but the tie layer thickens proportionately less than the top layer does toward the web edges. During the measurement series, ten spectra were taken at the seven-inch position, and ratios from all ten spectra are included in Figure 9. These cluster together well in the figure, showing good reproducibility.

Collaboration with the Center for Crops Utilization Research

The Center for Crops Utilization Research (CCUR) is developing agricultural substitutes for petrochemicals, including soy-protein based polymers, which can be extruded or molded into various items.[11] Their interest in the TIRS unit was for monitoring physical properties of the soy polymers during their compounding extrusion. The on-line tests were performed in May 2003 with the cooling-jet version of TIRS, and the tensile strength of a soy-protein polymer containing a modified rubber additive (polyisoprene-graft-maleic anhydride) was measured. Figure 10 shows the extruder and monitor in operation.

The tensile strength of the polymer was changed by altering both the amount of rubber additive (2, 5, or 10 weight percent) and the extruder screw speed. Reference values for the tensile strength were determined by CCUR staff, in accordance with ASTM Standard Test Method

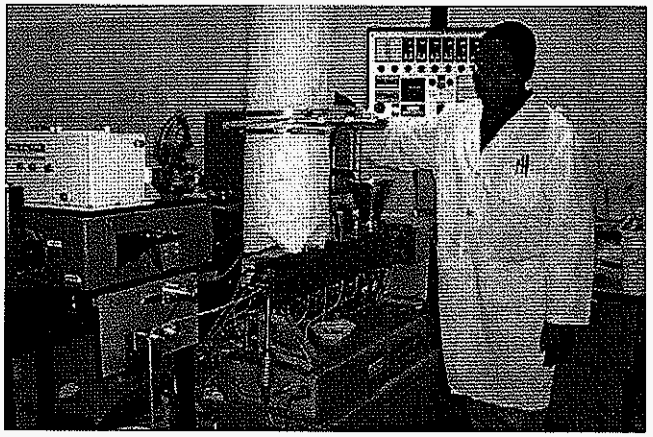

Figure 10. Dr. Mungara of the CCUR running the extruder as it produces soy-protein polymer, which the TIRS unit then analyzes.

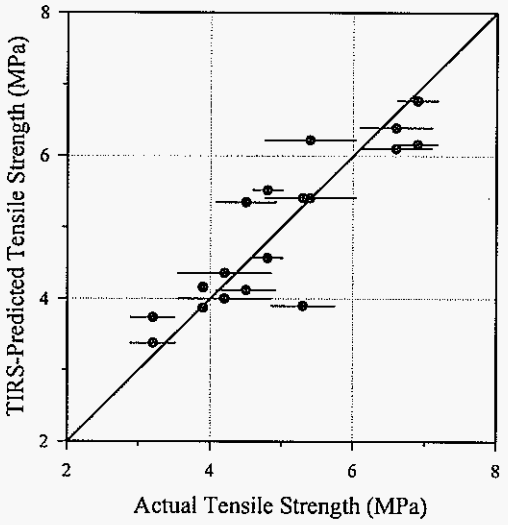

Figure 11. Cross validation between the TIRS and off-line measurements of the tensile strength of the extruded soy-protein polymer.

D638-86, using compression-molded sheets produced from the material extruded during the TIRS tests. Five samples were tested, and their results were averaged for each combination of additive concentration and screw speed. Two TIRS measurements were taken at each combination. Figure 11 shows the cross-validation correlation between the TIRS determinations and the off-line measurements. The SECV is 0.55 MPa. The bars show the error for the off-line measurements. Because two TIRS measurements were made at each setting, the plotted points appear as horizontally aligned pairs. The vertical separation between points in a pair indicates the reproducibility of the TIRS measurements, which is slightly larger than the off-line error.

Conclusion

TIRS has been successfully applied to three different processing lines, each with its own special demands, as part of this project. TIRS has previously been applied to several other widely disparate process lines monitoring tasks,[3-5] including cure of ultraviolet-cured acrylic coatings on polycarbonate films, cure of oven-cured polyurethane, cure of jackets on fiber-optic strands, and compositional analysis of molten extruder streams. TIRS is clearly a feasible approach to on-line monitoring for a wide variety of process lines.

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